

# REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words)  Elemental parameter sets have been completely developed and validated for sulfur (S), silicon (Si), and phosphorous (P). Results are much superior to those older semiempirical treatments. Extensive work has been completed on SAM1 parameters for iron (Fe), although final results are not available. Substantial obstacles have been overcome in the work and a clear route to the objective has been established. The theoretical framework is in place and all that is required is completion of the parameterization process. The experience we have gained will allow us to parameterize SAM1 for other transition metals very quickly. Iron parameters are currently in <i>beta</i> testing in a number of labs.					
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# I. Objectives and Significance

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The objective of the proposed research is to expand and implement a new semiempirical method, SAM1, that will explicitly include treatment of *d*-orbitals.

## II. Statement of Work (from original proposal)

### Year 1:

1. Prepare literature base and update MBSP for S, P, and Fe.
2. Parameterize SAM1 for S, P, and Fe.
3. Test and evaluate parameters.
4. Apply SAM1 to problems of chemical interest for S, P, and Fe.
5. Prepare and present results at ACS meeting.
6. Submit results for publication in the scientific literature.

### Year 2:

1. Prepare literature base and update MBSP for Cu, Ni, and Pt.
2. Parameterize SAM1 for Cu, Ni, and Pt.
3. Test and evaluate parameters.
4. Apply SAM1 to problems of chemical interest for Cu, Ni, and Pt.
5. Prepare and present results at ACS meeting.
6. Submit results for publication in the scientific literature.

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## III. Work Completed

### *Changes in Parameterization Philosophy and AMPAC Modifications*

Major modifications to the AMPAC program itself were required in order to commence the research. This was largely due to two complications introduced by the *d*-orbitals, especially as they were applied to transition metals.

Parameterization Philosophy: An *implicit* piece of data that has always been included in the parameterization process is the spin multiplicity of the

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system. Unless otherwise specified on the keyword line, AMPAC assumes this value to be "1" or a singlet state. In closed shell systems from the main group section of the Periodic Table, this is a safe assumption in virtually all cases. (Not always though: note that the ground state of O<sub>2</sub> is a triplet and this must be accounted for in the input file.) The correct spin MUST however be accounted for if the parameterization is to have any chance of success, as the  $\Delta H_f$ , IP,  $\mu$ , and geometry are all referenced to this ground spin state. The correct spin state must now be added *explicitly* for the parameterization procedure. There are two sources of data from which spin states may be obtained: molecular spectroscopy and *ab initio* calculations. We were forced to very carefully choose the molecules for the MBSP to maximize our access to experimental spin state data. When this data was not available for a molecule needed in the MBSP, higher level calculations were carried out to obtain the most stable spin state. GAUSSIAN92 with DFT program for this purpose, employing both DFT with double- $\zeta$  basis sets and HF calculations with double- $\zeta$  effective core potential basis sets was used for this purpose.

In addition to the difference in use of multiplicities in parameterization, the parameterization program itself was overhauled extensively. It was altered in order to incorporate the expanded CI needed for the transition metals (see below) and to incorporate a number of new optimization technologies to enable searches on the much more delicate parameter hypersurface found in transition metal parameterization.

AMPAC Modifications: The transition metal systems are the first cases where configuration interaction (CI) is used *during the parameterization process* in the Dewar-style methods. We hope that this will allow the parameters to relax around better values as much of the correlation energy (an important consideration in these systems) will be incorporated in the CI description and will not need to be "taken up" by the parameters themselves. Also, we determined that a modified and expanded version of AMPAC's configuration interaction (CI) module would be required to allow us to handle the greatly expanded spin state and orbital symmetry problems inherent to transition metal chemistry. So, an extensive re-coding of AMPAC to handle very large open-shell multiplicities was carried out before any real research could be done on the transition metal systems. This basically required the programmatic implementation of a "smart CI", an important consideration in future work

with transition metal systems. We have added a segment of program code that will predict which MO's are occupied by electrons and need to be mixed to obtain a proper quantum mechanical description and suggest that pattern to the user in terms of standard AMPAC keywords (*i.e.* TRIPLET, OPEN, C.I., etc.). The user will obviously be able to override these default values if the need arises. At present, we intend to use the "natural" first guess from AMPAC to commence the SCF procedure for suggesting the CI mixing pattern. In this approach, the RHF wavefunction from which the microstates are constructed for subsequent mixing is one where orbital occupancy and degeneracy patterns are well-defined. Use of CI in this fashion will automatically produce the most stable spin state as predicted by the SAM1 model by ranking the various spin states by energy. So, after the parameters are derived, the need to know the spin state of the system to a high degree of surety will be relieved.

While it may seem from the above that much time was wasted in "simply writing programs" and not doing science, this is not the case. The tools must be prepared and maintained for our research just as a experimentalist must take the time to set up and tune his instrument. Programming and system maintenance is our equivalent of this process.

#### *SAM1 Parameters for New Elements*

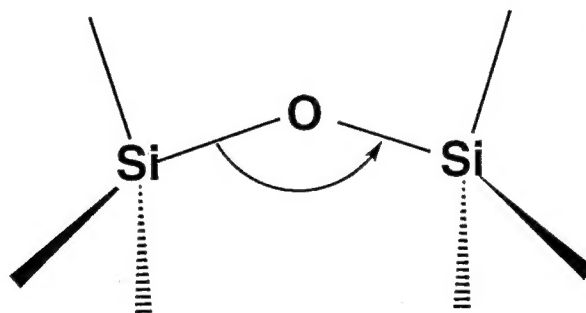
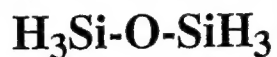
Main Group: Parameters for silicon (Si), sulfur (S), and phosphorous (P) were completed first, as data containing these elements was needed for additional parameterizations with the transition metals. The results are excellent, illustrating the both the efficacy of our improved parameterization program and the importance of the use of *d*-orbitals in treatment of the heavy main group elements. The representative results for each element is presented below, but a few general comments are certainly applicable. First, the predicted properties of hypervalent systems are substantially improved for all the elements. (This is a major goal of our work, since we hope to aid chemists in studying surface effects and catalysis, environments where hypervalency is common.) Second, the overall errors for the elements are generally lower than before. (This is especially the case for ionization potentials, which are a direct measure of the molecular orbital picture of the

molecules. Improvement in prediction of this property indicates that we have a better quantum mechanical model than previously.) Third, the standard deviation of the errors has also decreased substantially. In practical terms, the second and third improvements greatly increase the "trust quotient" of the method when applied to problems outside of the MBSP.

## Silicon

Property	# Species	Errors:		
		SAM1	AM1	PM3
$\Delta H_f$ (kcal)	62	6.09	7.33	6.56
$\mu$ (D)	20	0.36	0.41	0.75
IP (eV)	43	0.54	0.58	0.77

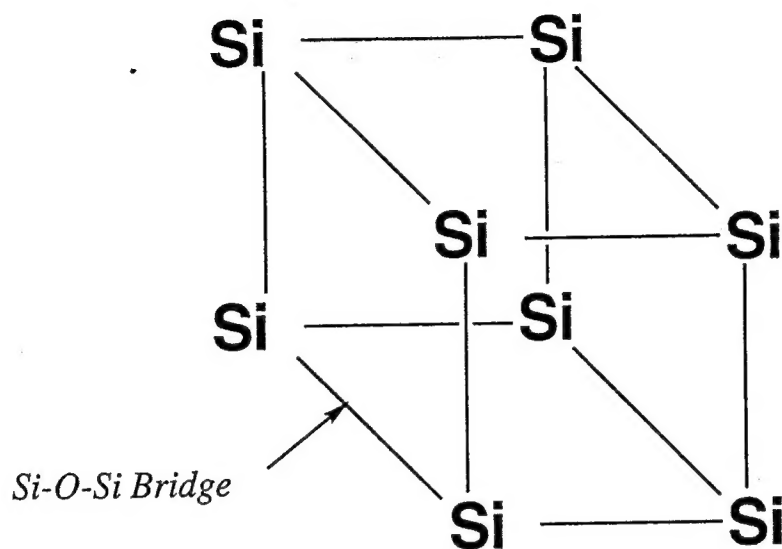
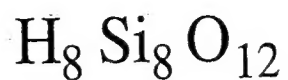
## Silicates



## Calculated Geometric Results

Item	AM1	SAM1	Expt'l
Si - O	1.728	1.605	1.634
Si - H	1.455	1.486	1.486
Si - O - Si	151.6	146.6	144.1

# *The "Cube"*



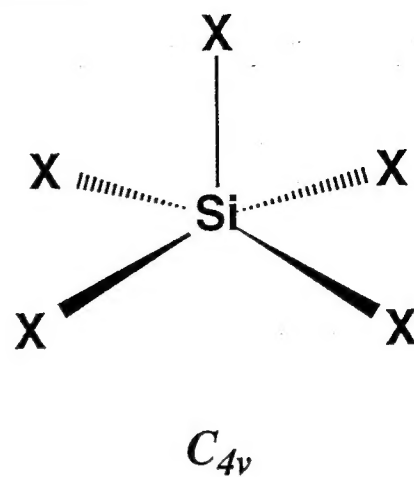
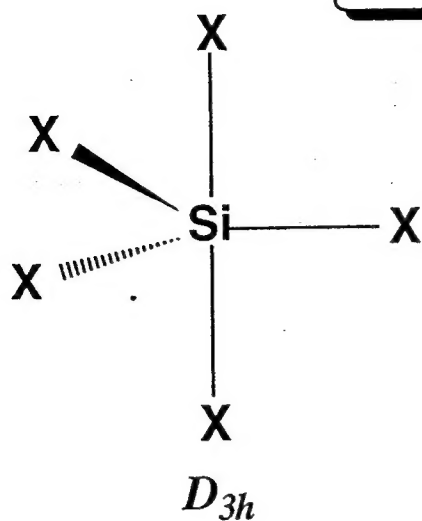
## *Calculated Geometric Results*

<u>Item</u>	<u>AM1</u>	<u>SAM1</u>	<u>6-31G*</u>	<u>Expt'l</u>
<i>For H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub></i>				
Si - O	1.709	1.605	1.634	1.619
Si - H	1.455	1.486	1.486	—
Si - O - Si	151.6	146.6	144.1	147.5
O - Si - O	105.8	108.0	109.0	—

## *Errors for Si Polyhedra (n = 4, 6, 8, 10, 12)*

Si - O	+0.08	-0.03	—	—
Si - H	-0.02	+0.03	—	—
Si - O - Si	+7.6	+2.6	—	—
O - Si - O	-3.0	-1.3	—	—

# Conformers of $\text{SiX}_5$



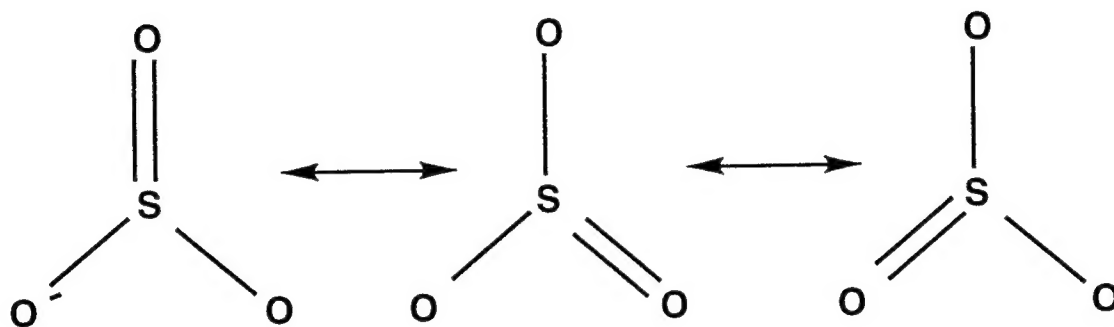
<u>Energy<sup>1</sup></u>	<u>SAM1</u>	<u>AM1</u>	<u>PM3</u>	<u>HF/6-31G*</u>	<u>Expt'l</u>
<i>X = Hydrogen</i>					
$D_{3h}^*$	17.0*	25.0*	55.8*	—*	20.6*
$C_{4v}$	19.2	27.4	90.8	—	—
$\Delta\Delta H_f$	-2.2	-2.4	-35.0	-4.2	—
<i>X = Fluorine</i>					
$D_{3h}$	-505.0*	-503.5*	-504.4*	—*	-505.5*
$C_{4v}$	-500.2	-501.6	-502.9	—	—
$\Delta\Delta H_f$	-4.8	-2.9	-1.5	-4.2	—
<i>X = Chlorine</i>					
$D_{3h}$	-249.0*	-267.6*	-173.1*	—*	-235.7*
$C_{4v}$	-244.6	-265.1	-170.6	—	—
$\Delta\Delta H_f$	-4.4	-2.5	-2.5	-4.4	—

1. kcal/mol.

# Sulfur

Property	# Species	Errors:		
		SAM1	AM1	PM3
$\Delta H_f$ (kcal)	76	6.45	7.09	9.33
$\mu$ (D)	45	0.40	0.49	0.59
IP (eV)	67	0.39	0.33	0.39

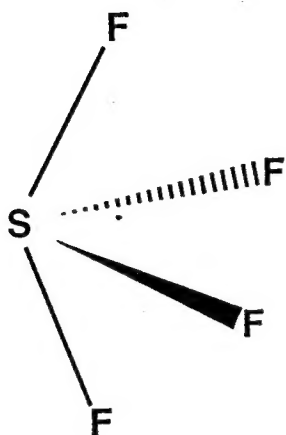
## SO<sub>3</sub> (Sulfur Trioxide)



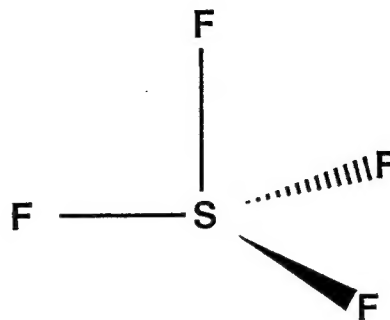
Item	SAM1	AM1	PM3	Expt'l	Degen.
$\Delta H_f$	-100.0	-97.3	-104.7	-94.5	-
S - O	1.42	1.35	1.38	1.43	-
Sym. Bend	458	437	421	495	1
Asym. Bend	477	460	401	529	2
Sym. Str.	1095	928	772	1068	1
Asym. Str.	1363	1261	1070	1391	2



$SF_4$   
(Sulfur Tetrafluoride)



$C_{2v}$



$C_{3v}$

<i>Item</i>	<i>SAM1</i>	<i>AM1</i>	<i>PM3</i>	<i>RHF/6-31G*</i>	<i>Expt'l</i>
$\Delta H_f, C_{2v}$	-179.5	-225.5	-192.3	—	-182.4
$\Delta H_f, C_{3v}$	-152.5	-221.3	-185.3	—	—
$\Delta \Delta H_f$	-27.0	-4.2	-7.0	-34.4	—
(For $C_{2v}$ )					
S — F <sub>ax</sub>	1.68	1.57	1.62	1.63	1.65
S — F <sub>eq</sub>	1.53	1.55	1.60	1.54	1.54
$\Delta(\text{Ax.} - \text{Eq.})$	0.15	0.02	0.02	0.09	0.11
F <sub>ax</sub> SF <sub>ax</sub>	166.6	170.4	142.3	170.0	173.1
F <sub>eq</sub> SF <sub>eq</sub>	102.4	103.7	121.2	102.6	101.6

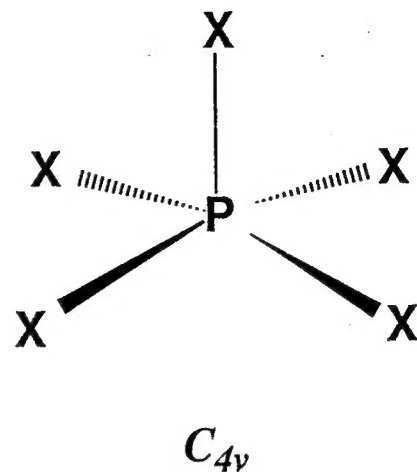
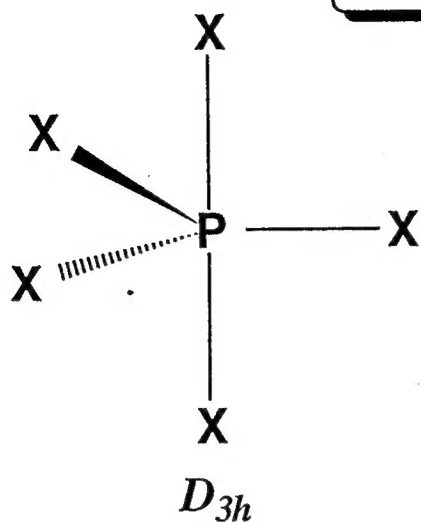
## Phosphorous

Property	# Species	Errors:		
		SAM1	AM1	PM3
$\Delta H_f$ (kcal)	60	9.97	16.63	15.82
$\mu$ (D)	17	0.66	0.99	1.02
IP (eV)	38	0.69	0.84	0.93

## Reactions

<i>Process</i>	<i>6-31G*</i>	<i>6-31G(2df)</i>	<i>AM1</i>	<i>PM3</i>	<i>SAM1</i>	<i>Expt'l</i>
$2 \text{ P}_2 \longrightarrow \text{P}_4$	-32.7	-44.2	1.2	-21.1	-59.7	-55.0
Inversion of $\text{PH}_3$	37.8	34.4	32.8	22.6	34.0	31.5

# Conformers of $PX_5$



<u>Energy<sup>1</sup></u>	<u>SAM1</u>	<u>AM1</u>	<u>PM3</u>	<u>HF/6-31G*</u>	<u>Expt'l</u>
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*X = Fluorine*

$D_{3h}^*$	-384.3*	-379.3*	-386.9*	-*	-381.0*
$C_{4v}$	-379.3	-376.6	-382.8	-	-
$\Delta\Delta H_f$	-5.0	-2.7	-4.1	-5.6	-

*X = Chlorine*

$D_{3h}$	-100.3*	-71.8*	-111.6*	-*	-89.6*
$C_{4v}$	-93.5	-68.0	-109.2	-	-
$\Delta\Delta H_f$	-6.8	-3.8	-2.4	-5.8	-

*X = Iodine*

$D_{3h}$	-21.9*	53.0*	-27.1	-	-11.0*
$C_{4v}$	36.4	69.2	-27.2*	-	-
$\Delta\Delta H_f$	-58.3	-16.2	0.1	-	-

1. kcal/mol.

Transition Metals: At present, the only transition metal parameters we have completed are those for iron (Fe). We chose this element as our starting point because of the high interest in its chemistry and the (hopefully) abundance of data in the literature for parameterization. It was perhaps an unfortunate choice in that the compounds of iron have a variety of possible spin states. There is also little experimental data to suggest which is the most stable state, so the necessity of doing extensive *ab initio* calculations slowed down work somewhat. The first version of the parameters has been released in the AMPAC program and is now being *beta* tested by a large group of users in a variety of contexts. The results are generally encouraging.

It should be noted that we have not yet published a methodological paper for SAM1 in the open chemical literature. We have been criticized for this in some circles, but I should point out that the reason we have withheld this publication is that the method is still subject to modification. As we proceed toward our first certified set of parameters for an element that has open *d*-orbitals in the valence manifold (iron), we are still altering the theoretical details of the method. Until we have settled all of the several open questions, we will not publish a paper describing the method. We expect to have the method paper in the literature by year's end.